



New Engineering Polymer Systems Using High Throughput Modeling Techniques

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14. ABSTRACT <p>This project focused on the development of a high-throughput Polymer Discovery Tool (PDT) by expanding Group Interaction Modeling (GIM) and validating it across a range of high performance epoxy resins and epoxy resin blends with amine hardeners. The project achieved its targets, which included: (i) the development of the first high throughput version of the Polymer Discovery Tool, (ii) the successful implementation and validation of the prediction of thermomechanical properties against experimental data, (iii) the identification of suitable methods and tools to use in the software implementation of the model and website and (iv) the further development of the model to incorporate other classes of polymers such as but not restricted to: other thermosetting polymers, thermoplastics or semi-crystalline systems. The software allows the user to see animated simulations of the property evolution against any descriptor. This efforts results have been presented at the following forums:</p> <p>1) Thermosets 2015 (16 - 18 September 2015, Berlin, Germany), presentation in the Modelling and Characterisation session.</p> <p>2) O.A. Amariutei, J.P. Foreman, High performance epoxy resin design using group interaction modeling, Thermosets 2015 - From Monomers to Components: Proceedings of the 4th international Conference.</p> <p>3) Dynamic Materials and Interactions Portfolio Review Meeting 2015 (11- 13 August 2015, Fort Walton Beach, FL, USA), presentation on Informed Materials Discovery: Designing New Engineering & Polymer Systems Using High Throughput Modelling Techniques.</p>					
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1. STATUS OF EFFORT

To date the project has achieved all of its targets. These include: (i) the development of the first high throughput version of the Polymer Discovery Tool, (ii) the successful implementation and validation of the prediction of thermomechanical properties against experimental data, (iii) the identification of suitable methods and tools to use in the software implementation of the model and website and (iv) the further development of the model to incorporate other classes of polymers such as but not restricted to: other thermosetting polymers, thermoplastics or semi-crystalline systems.

The report is organised as it follows: Section 2 highlights the projects achievements, their significance to the field, their relationship to the original goals and their potential applications; Section 3 breaks down the detailed overview in Computational and Scientific achievements; and Section 4 summarises the dissemination activities. The deviations from the original proposal have been included and the reasons have been described. The additional work undertaken but not included in the initial proposal has been outlined, providing the background to their inclusion.

The project has ended under the premises of a 3 years continuation, which started on 1st of July 2015.

2. ACCOMPLISHMENTS

- The first high-throughput version of the Polymer Discovery Tool (PDT) has been successfully implemented by expanding Group Interaction Modelling (GIM). PDT v1.0 has been tested and validated for a range of high performance epoxy resins and epoxy resin blends with amine hardeners. The high-throughput thermo-mechanical property (loss tangent, volume and density, bulk modulus, stress-strain curves, etc.) prediction of the epoxies implemented is in very good agreement with the experimental results.
- The high-throughput implementation computes data in tabular format, predicting full mechanical properties (tensile, shear and bulk elastic moduli) as well as the dynamic thermo-mechanical spectra, beta and glass transition temperatures and the associated loss tangent against user specified parameter(s). The PDT v1.0 has been implemented with near future expansion of the software and molecule database in mind. The current computational framework can incorporate further properties and additional modelling modules as required.
- The software has two operation modes, depending on the user and purpose. The unsupervised operation mode, although lengthier, runs on a combinatoric logic, matching all the structures found in the database in various proportions and computing a ranking based on their predicted properties. The properties of each molecular combination can be viewed and inspected against various parameters, such as temperature, strain rate, degree of cure, etc. The supervised mode, works as a focus tool and enables the user to explore in detail a particular polymer system and/or set of properties.
- The developed high-throughput model has been utilised to investigate the effect of different chemical (composition), physical (cross-linking) and structural factors on the final properties and performance of epoxy resin systems. The multi-scale approach provides the material designers with the ability to eliminate the time consuming trial-and-error steps from the epoxy resin formulation process.
- Ternary high performance epoxy systems have been investigated with the help of the newly implemented high throughput version of GIM. By systematically varying the chemical composition of the epoxy ternary systems, the loss/gain in properties has been observed and the driving parameters have been discussed.
- Combining experimental and theoretical approaches, the PDT v1.0 tool was used in exploring the beta transition in epoxy resins. The beta transition has been tailored by altering the resin chemistry and observing the impact this has. In particular, the inherent toughening that the beta transition provides is investigated with a view to developing high performance resins which need less toughening agent added when in use.

3. OVERVIEW

Group Interaction Modelling (GIM) provides a multi-scale framework for predicting the complex mechanical properties of polymers through a series of predictive analytical equations. Unlike phenomenological models with high numbers of fitting parameters, the independently calculated thermo-mechanical properties in GIM do not have to be obtained by fitting the experimental data they are trying to predict. GIM is designed to complement detailed numerical molecular dynamics calculations where high computational costs restrict both the time and length scales of the simulations.

Informed and novel materials discovery is possible by combining GIM with intelligent data mining and database construction. A High Throughput (HT) development of GIM is a simple, yet powerful concept: create a large polymer database of mer units containing descriptors of their chemical structures, generate a database of the calculated thermomechanical properties of existing and hypothetical materials, and then intelligently interrogate the database in the search of materials with the desired properties.

The practical implementation of the HT GIM requires 4 steps:

- (i) **chemical structure database:** building up a database of components characterised by their structural unit;
- (ii) **property prediction:** thermomechanical property calculations of materials;
- (iii) **rational materials storage:** systematic storage of the information in database repositories;
- (iv) **materials characterisation and selection:** data analysis aimed at selecting novel materials or gaining new physical knowledge.

All 4 stages are linked and necessary, but the last one is the most challenging and potentially rewarding. Extracting the relevant information from a vast database of properties, requires a deep understanding of the problem at hand. The intelligent ranking, comparison, and searching of a database is implemented by means of "descriptors". These are empirical quantities, not always observable, connecting the calculated mer unit parameters (e.g. crosslinking) to material properties (e.g. modulus).

Once a good descriptor is identified, the search for better materials within the repository can be performed intrinsically or extrinsically, depending on whether the optimum solutions are already included in the set of calculations or not. Intrinsic searches include just step (iv), require only fast descriptors, and may employ various informatics techniques. Extrinsic searches involve all four steps, as the search for an optimal solution implies iterations leading to an expansion of the repository. The extrinsic implementation of HT GIM will include (in the next three years) an important component: a computational expansion capable of using the evaluation of descriptors on existing database entries to guide new calculations not yet included in the database. This feature is the crucial component in achieving a Polymer Discovery Tool.

3.1. Group Interaction Modelling (GIM). Whilst the molecular mechanics and dynamics are becoming a standard tool for hierarchical polymer characterisation, the time, temperature and length scales are not easily applicable to real engineering problems [1, 2]. Continuum level descriptions of polymer properties have been investigated in the literature to describe the macroscopic and microscopic responses of polymers. Continuum models are classified into thermodynamic consistent and phenomenological approaches. In terms of phenomenological approaches, which are based upon spring and dashpot elements one may mention works by [3, 4, 5, 6]. The main deficiency associated with these continuum level modelling approaches is the high number of material parameters which need to be found through calibration process between simulations and experimental data. In the case of molecular level models, most recently a plasticity theory was developed by considering the rate dependence of the glass and beta transition loss peaks and storage modulus in PC and PMMA [7].

The GIM framework provides a multi-scale approach which is developed based upon the premise that the macroscopic mechanical responses of polymers are a direct consequence of energy stored and dissipated at the molecular level during a thermomechanical loading [8, 9, 10, 11, 12]. The energetic description for the deformation mechanisms in polymers is originated in the works by [13, 14, 15] and it is generalised in GIM in order to incorporate the molecular chemistry and molecular physical structure into the prediction of the macroscopic constitutive properties and behaviour of the polymers.

GIM uses a mean field potential function approach to predict the structural (thermal, volumetric and mechanical) properties of polymers. The method uses a simple contribution based approach to calculating the total energy of the system. Interactions between neighbouring polymer chains are defined using a potential function that consists of several thermodynamic energy terms:

$$(1) \quad E = E_{coh} \left(\left(\frac{V_T}{V} \right)^6 - 2 \left(\frac{V_T}{V} \right)^3 \right) = -E_{coh} + H_C + H_T + H_M$$

Equation (1) represents the equation of state for the system. The total energy of the system, E is expressed as a potential energy well of depth ϕ_0 (ϕ_0 is the molecular potential energy well depth which translates to the molar quantity E_{coh}) and is based upon a standard Lennard-Jones potential function using the volume V . The volume of the mer unit is defined as $V = \pi r^2 L$, where r is the separation distance between chains and L is the length of the mer unit. In bulk model terms, the total energy is comprised of cohesive E_{coh} , thermal H_T , mechanical H_M , and configurational contributions H_C . The configurational energy H_C in GIM is calculated based upon the level of the cohesive energy for different configurations. The thermal energy H_T , is correlated to the molecular level temperature variations through heat capacity C , while the mechanical energy H_M , is calculated based upon the volumetric changes $\Delta V/V$, and the shearing strain γ , and it is dependent on the bulk, B' , and shear, G' , moduli of the body.

The heat capacity in GIM identifies the thermal energy term which captures the molecular level skeletal mode vibrations and contributes to the temperature dependent mechanical properties of polymers. The heat capacity, i.e. C , in GIM is discretised into a sum of three main terms: C_b , C_β and C_g , which are respectively heat capacities associated with the background, beta and glass transitions. A simple approach a one-dimensional Debye function of skeletal mode vibrations is utilised to describe the background heat capacity, C_b , in terms of number of the background degrees of freedom (DOF) per group, N , the reference temperature of cooperative skeletal vibrations, θ , and the temperature, T . The C_β and C_g are related to the loss of DOFs over beta and glass transitions, where R is the molar gas constant and C is defined by:

$$(2) \quad C = NR \frac{\left(\frac{6.7T}{\theta_1}\right)^2}{1 + \left(\frac{6.7T}{\theta_1}\right)^2}$$

The GIM method uses this energy relation as a basis to derive predictive equations for structural properties. In order to quantify the energy terms, a series of fundamental quantities are required that relate the energy terms to the structure of the polymer. Several fundamental parameters are required as input into GIM and are based on the representative mer unit. These are the degrees of freedom, N , the cohesive energy at absolute zero, E_{coh} (0 K), the van der Waal's volume, V_w , the length, L , the molecular weight, M , and the Debye temperature, θ_1 .

The parameters are well defined and constant for each mer unit, though the variation of N with temperature through the two transitions is of importance later. The values of these parameters can be obtained from a variety of sources, including contribution tables, connectivity indices or molecular modelling. Initial values are taken from group contributions such as those shown in Figure 1, where highlighted in orange and mauve are the phenyl ring and epoxy group contributions. Equilibrium volumetric properties such as density and volumetric expansion coefficients, α , are calculated by solving equation (1) as a quadratic equation in $(V/V_0)^3$ as a function of temperature. In a similar approach further properties can be derived: for example hydrostatic pressure, P , is calculated as a function of volume using the differential of the potential function of equation (1) and the pure elastic form of bulk modulus, B_e , is calculated as a derivative of energy or pressure:

$$(3) \quad P = \frac{dE}{dV} = \frac{6E_T}{V_T} \left(\left(\frac{V_T}{V}\right)^4 - \left(\frac{V_T}{V}\right)^7 \right)$$

$$(4) \quad B_e = V \frac{dE^2}{dV^2} = \frac{6E_T}{V_T} \left(5\left(\frac{V_T}{V}\right)^4 - 8\left(\frac{V_T}{V}\right)^7 \right)$$

Group	N	E_{coh} (J/mol)	V_w (cm ³ /mol)
CH ₂	2	4500	10.25
Phenyl	3	25000	43.3
N	2	9000	4
Epoxy	4	15300	22
CH(OH)	2	20800	11.5
SO ₂	2	45000	20.3
TGDDM Mer Unit	36	191700	232.9
TGAP Mer Unit	25	129700	148.3
DDS Mer Unit	12	113000	114.9
TGDDM/DDS	24	152350	173.9
TGAP/DDS	19	121116	134.0

FIGURE 1. Mer units based on functional group contributions for two high performance epoxy systems: tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) and triglycidyl-*p*-aminophenol (TGAP) cured with diaminodiphenyl sulfone (DDS). DDS is illustrated in the diagram as either 4,4-DDS in black or 3,3-DDS in grey.

3.2. Computational achievements. In the past 12 months the Polymer Discovery Tool has been developed from a single input set of data to fast, high-throughput predictive model for a series of high performance epoxy resin systems.

Amine cured multifunctional epoxy resins exhibit a high degree of crosslinking when cured leading to an amorphous 3D network architecture. This structure gives the resins a combination of high strength, stiffness and other properties desirable for the matrix phase in composite systems. GIM is ideal for predicting the properties of such polymers as the crosslinking can be included as a reduction of the degrees of freedom at a molecular level.

Properties ranging from internal energies, volume (and density), heat capacity, engineering moduli (and Poisson's ratio) and the stress-strain curve are predicted accurately and quickly, exposing the material performance at a glance. The properties are predicted not only as a function of temperature, pressure and strain rate but also as a function of other user defined parameters. The blends of epoxies and hardeners implemented so far have been validated against experimental data, where available. Part of the experimental data has been collected from scientific literature and part from experimental work performed locally. The Polymer Discovery tool has been tested using resin composition as a key variable (e.g. percentage of epoxy resin and hardener in a simple binary system followed by multiple resins and hardeners). As it stands, the software has been implemented in MATLAB and it has an interactive user interface. The in house database of molecules currently includes 5 epoxy resins and 9 hardeners. The interactive menu facilitates both supervised and unsupervised prediction of properties, of the whole database or just a restricted selection. The software can be used in a virtual combinatorial manner, allowing multi epoxy blends. The property prediction yields data in tabular format and a few

default graphic representations of properties. For the informed user, the software facilitates further statistical investigation and comparison of the properties.

3.3. Scientific achievements. In this work the property optimisation process for development of high performance epoxy resin systems is carried out by developing a high-throughput version of GIM. The chemical structure and the molecular composition of epoxy resin are varied systematically to evaluate their effect on different thermomechanical properties of the epoxy system. The rate and pressure dependency of the material properties are also captured through the developed multiscale framework which provides a full optimisation map for high performance epoxy resin development. The optimisation maps may help to replace the traditional time consuming approaches for the polymer manufacturing. For example, in the case of Quantitative Structure Property Relation (QSPR) approach, the polymer properties are directly related to their chemical composition and morphology through molecular models, e.g. the group contribution approach [16, 17]. The main difficulty in QSPR approach is in the case of novel polymers where the relationships between new polymer chain structure is not well-understood [18]. GIM provides a self-consistent approach which fills the gap between the simple QSPR approach and the computationally expensive molecular dynamic framework in which the engineering property parameters for component are understood quantitatively in terms of their chemical and morphological structure.

For example, Figure 2 depicts the effect on the network density of: crosslinking (left) for a 50-50 TGDDDM TGAP cured with DDS system and degree of cure (right) on a a 50-50 TGDDDM TGAP cured with DDS system, while Figure 3 characterises density dependent on chemical composition by varying the fraction of TGDDDM and TGAP inverse proportionally by 20% (left) at a constant strain rate of $\dot{\epsilon} = 1\text{Hz}$, and the effect of strain rate (right) for a 50-50 TGDDDM/TGAP cured with DDS.

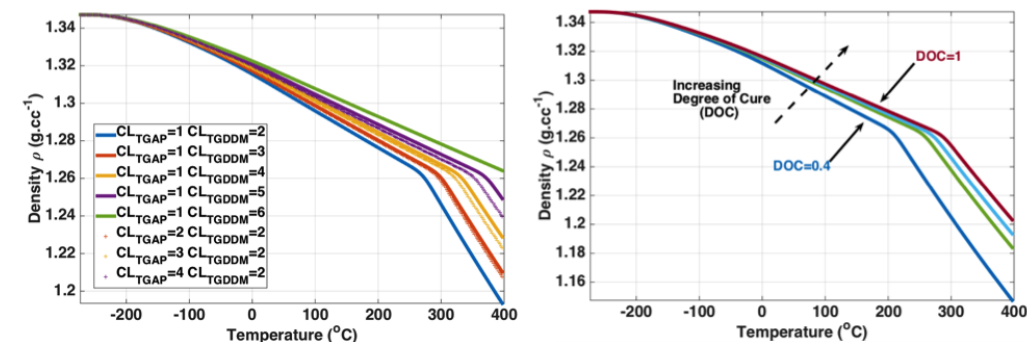


FIGURE 2. Effect of crosslinking and degree of cure for a TGDDDM/TGAP-DDS system.

In a virtual combinatorial approach, the new high-throughput implementation allows the investigation of ternary epoxy blends. Using a ternary plot, and a wide range of descriptors (T_β , T_g , degree of cure, strain rate, price ..etc) the user can make informed decisions regarding the design of the epoxy system. The software allows the user to see animated simulations of the property evolution against any

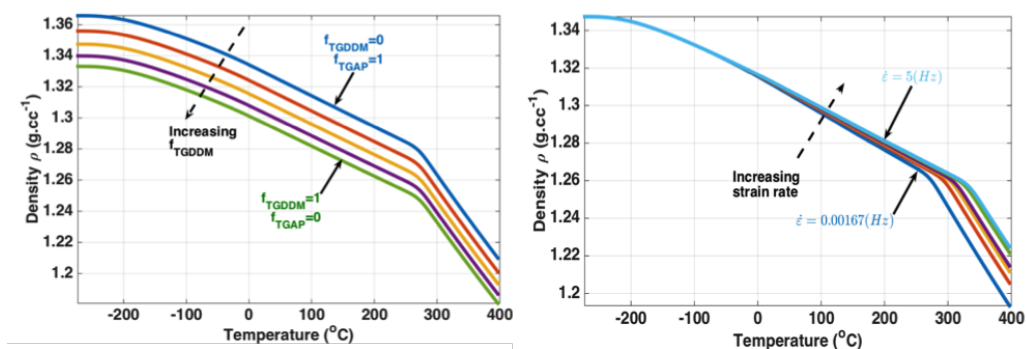


FIGURE 3. Effect of chemical composition and strain rate on density for a TGDDM/TGAP - DDS system.

descriptor. Below, Figure 4 shows the distribution of T_g and density on a ternary blend (DGEBA/TGAP/TGDDM cured with DDS) at $T=189^\circ\text{C}$ and $T=239^\circ\text{C}$.

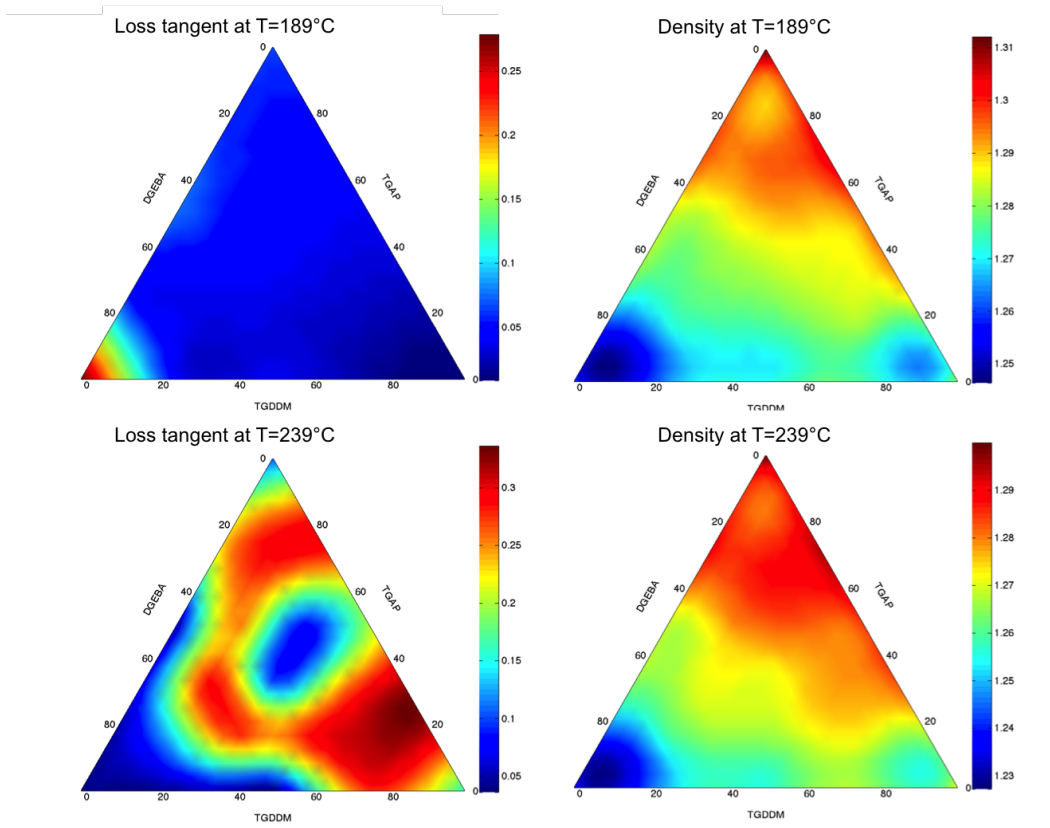


FIGURE 4. Ternary epoxy systems cured with 4,4' DDS, showing the T_g at $T=189^\circ\text{C}$ and $T=239^\circ\text{C}$ in left panels and Density at $T=189^\circ\text{C}$ and $T=239^\circ\text{C}$ in right panels.

4. TRANSITIONS/PUBLICATIONS

- Thermosets 2015 (16 - 18 September 2015, Berlin, Germany), presentation in the "Modelling and Characterisation" session.
- O.A. Amariutei, J.P. Foreman, High performance epoxy resin design using group interaction modeling, Thermosets 2015 - From Monomers to Components: Proceedings of the 4th international Conference.
- Dynamic Materials and Interactions Portfolio Review Meeting 2015 (11-13 August 2015, Fort Walton Beach, FL, USA), presentation on "Informed Materials Discovery: Designing New Engineering & Polymer Systems Using High Throughput Modelling Techniques".

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